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CASTING OF HALIDE AND FLUORIDE ALLOYS FOR LASER WINDOWS

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J. Pappis

Raytheon Research Division
Waltham, Massachusetts 02154

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Infrared Materials,
Alkaline Earth Fluorides,
Casting
Strontium Fluoride
Optical Properties,
Mechanical Properties,
Calcium Fluoride

micrometer

20. ABSTRACT (Continue on reverse side if necessary and identify by block number) During the third quarter of this program high quality castings of both CaF_2 and SrF_2 were fabricated regardless of the starting material. That is, either high purity single crystal chips or pre-treated "reagent" grade powder can be used to yield equivalent castings. The calorimetrically measured 5.25μm apparent absorption coefficient of cast CaF_2 has been consistently attained near ~~4.5×10^{-4}~~ cm^{-1}. For cast SrF_2, the 5.25μm absorption coefficient lies near ~~$3.5 \times 10^{-5} cm^{-1}$~~ after correcting for surface loss. Preliminary work was begun in developing procedures for casting and annealing the alkaline earth fluorides in an inert atmosphere.

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Abstract (Cont'd.)

Mechanical measurements on cast CaF_2 show average fracture strengths ranging from a minimum near 6600 psi to near 23000 psi, depending on both the quality of polished surfaces and whether or not the polished samples are annealed prior to testing. This dependence is evidence that fracture is limited by surface flaws. Preliminary results for cast SrF_2 show similar results with average fracture strengths being equivalent to cast CaF_2. Originator Supplied Keywords include:

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TECHNICAL PROGRAM SUMMARY

The main objective of this program is to demonstrate the feasibility of fusion casting of alkali halides and alkaline earth fluorides for high power laser window applications. The main effort deals with the fabrication and property evaluation of the alkaline earth fluorides.

During the third quarter of this program high quality castings of both CaF_2 and SrF_2 were fabricated regardless of the starting material. That is, either high purity single crystal chips or pre-treated "reagent" grade powde- can be used as starting material to yield equivalent castings.

Castings of CaF_2 were attempted in an inert atmosphere of purified argon (1 - 50 torr). The advantage over vacuum casting is that unidirectional solidification is better accomplished because of the better heat transfer provided by the gas.

Preliminary hot forgings of polycrystalline cast CaF_2 were done at 1000°C. At the high temperature a large grain size results so that not much advantage in grain size reduction is gained.

Calorimetrically measured 5.25μm apparent absorption coefficients for cast CaF_2 are being consistently attained near $4.5 \times 10^{-4} cm^{-1}$ regardless of the starting material. Those castings of CaF_2 fabricated in an inert atmosphere (purified argon) have 5.25μm apparent absorption coefficients typically greater than $1 \times 10^{-3} cm^{-1}$, although one excellent casting was obtained ($4.1 \times 10^{-4} cm^{-1}$). Using surface loss corrections, the 5.25μm absorption coefficient of cast SrF_2 is near $3.5 \times 10^{-5} cm^{-1}$.

Mechanical measurements on cast CaF_2 show average fracture strengths ranging from a minimum near 6600 psi to near 23000 psi, depending on both the quality of polished surfaces and whether or not the polished samples are annealed at 900°C (a strain relief procedure) prior to testing. This dependence is evidence that fracture is limited by surface flaws. Preliminary results for cast SrF_2 samples show average fracture strengths equivalent to cast CaF_2.

PREFACE

This report was prepared by Raytheon Company, Research Division, Waltham, Massachusetts under Contract No. F19628-74-C-0148 entitled "Casting of Halide and Fluoride Alloys for Laser Windows." This work is supported by the Advanced Research Projects Agency and is monitored by the Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

At Raytheon the investigation is being carried out in the Advanced Materials Department under the direction of Dr. J. Pappis, principal investigator, and Dr. R. Newberg. Assisting with material fabrication and processing are T. Wong and A. De. Optical polishing is provided by R. Cosgro. Dr. T. Kohane and T. Varitimos are performing the laser calorimetry measurements. Dr. O. Guentert, W. Tye, and D. Howe are providing the SEM micrographs, microprobe analyses, and X-ray diffraction analyses. P. Roman is assisting with the mechanical property measurements. This report has been given an internal number of S-1817.

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1.0 INTRODUCTION

The primary objective of this program is to demonstrate the feasibility of fusion casting of alkali halides and alkaline earth fluorides for use as windows for high power lasers. In a previous program, initial work on alkali halide alloys, particularly $SrCl_2$-doped KCl, indicated that casting was a promising fabrication process.

The work on the alkaline earth fluorides is being stressed because they are more amenable to fabrication by fusion casting due to their smaller volume change on solidification and their better thermal and mechanical properties compared to the alkali halides, as was discussed in a previous report.[1] Therefore, this program investigates the effects of casting parameters and annealing procedures on the microstructure, mechanical properties, and optical properties of the alkaline earth fluorides. In addition, the effects of impurities and alloy additions on microstructure and properties are being evaluated. Equally significant is the study of the importance of starting materials and purification schemes on the optical absorption and scatter of the cast ingots.

2.0 RESULTS

2.1 Vacuum Casting

During the third quarter of this program, the main effort was directed toward the fusion casting of pure alkaline earth fluorides, divided about equally between CaF_2 and SrF_2, with the latter being stressed during the second half of the quarter. Both large vacuum furnaces were used, with most of the casting (46 runs) being done in the vacuum hot press (VHP) furnace capable of castings of about five and one-half inches in diameter. The two-zone (CF) furnace was used for casting (6 runs), annealing (19 runs) and purification of "reagent" grade powder (4 runs).

Tables I and II list all the runs performed in the two furnaces and include casting, annealing, purification, and hot forging runs. Figure 1 shows a polished three-inch diameter by about one-half-inch thick window of pure SrF_2 cast in the laboratory. The grain size of such castings is large and is typically on the order of 1 cm.

As mentioned above, nearly all of the castings were produced in the VHP furnace (an all graphite system). Late in the quarter, six runs were attempted in the two-zone furnace as listed in Table II. In this furnace, as was discussed in a previous report,[1] there has been a problem with the reaction of fluoride vapors both with the insulating supports for the molybdenum elements and with the thermocouple insulating tubes. However, these few runs demonstrated that the problem is associated only with CaF_2 and not with SrF_2; i.e., with the present castings of SrF_2 no such reactions occurred even though high temperatures (1475 - 1500°C) were used. The only remaining problem preventing successful vacuum casting of SrF_2 in this furnace is the poor vacuum capability (10^{-2} - 10^{-3} torr) provided by the mechanical vacuum pump system. A diffusion vacuum pump system has been ordered for installation during the fourth quarter.

At the beginning of the casting program for SrF_2, it was noted that the cast ingots were much more susceptible to cracking (probably from thermal shock) than are similar CaF_2 ingots. The problem was in general remedied

TABLE I

VACUUM HOT PRESS (VHP) RUNS
PURE FLUORIDES

VHP No.	Material	Comments
284, 285	SrF_2	Small castings; cracked
286 - 297	CaF_2	Large castings; good runs
300	SrF_2	Large casting; cracked
301	CaF_2	In argon 50 mm; colorless casting
302, 303	CaF_2	Hot forged samples (VHP-269) at 1000°C
304	CaF_2	In < 1 mm argon; bluish casting
306	CaF_2	In 5 mm argon; yellowish casting
307, 308, 309	CaF_2	From purified powder; castings cracked
311, 312	SrF_2	Fast cooled; castings cracked
313	CaF_2	In 15 mm argon; bluish casting
314	CaF_2	In 50 mm argon; yellowish casting
316	CaF_2	Small casting; intergranular cracks
317	CaF_2	Remelt VHP-309; In 50 mm argon intergranular cracks; colorless casting
318	CaF_2	In 50 mm argon; no cracks; yellow-blue casting
319 - 321	SrF_2	Trouble with power supply; no melting
324	CaF_2	Purification of powder plus two percent teflon
325	SrF_2	Purification of powder plus two percent teflon
326, 327	SrF_2	Cooled nominal 75°C/hr; cracked
329	SrF_2	Melt VHP-325; cooled 45°C/hr; cracked cloudy ingot (white precipitates)
332	SrF_2	Remelt 326; cooled 25°C/hr; good
333	CaF_2	Two crucibles in furnace; cooled 75°C/hr.
334	SrF_2	Cooled 15°C/hr; no good
335	SrF_2	Purified powder (vacuum baked); cooled 25°C/hr; good
338	SrF_2	Cooled 25°C/hr; white precipitates
339	CaF_2	Not melted
340	SrF_2	Cooled 60°C/hr; good casting
341	CaF_2	Cooled 75°C/hr; good
342	SrF_2	Cooled 25°C/hr; power failure; cracked
343	SrF_2	Remelt VHP-342; cooled 75°C/hr; good
344, 345	SrF_2	Cooled 75°C/hr; cracked
346	SrF_2	Cooled 45°C/hr; cracked
348, 349	SrF_2	Cooled 40°C/hr; good

TABLE II

TWO-ZONE FURNACE (CF) RUNS
PURE FLUORIDES

CF No.	Material	Comments
70-77, 79-81, 83-85	CaF_2	Annealing (900°C) cast ingots
82, 88, 89, 97, 98	SrF_2	Annealing (900°C) cast ingots
78	CaF_2	Powder purification in teflon vapors
86, 90	SrF_2	Powder purification in teflon vapors
87	SrF_2	Vacuum bake powder (900°C)
91	SrF_2	Casting failed because it did not melt
92, 93	SrF_2	Casting in teflon vapor partial pressure 50 - 100μm. Ingots clear but cracked
94 - 96	SrF_2	Casting in teflon vapor partial pressure 300 - 400μm. Ingots discolored (pink) and cracked

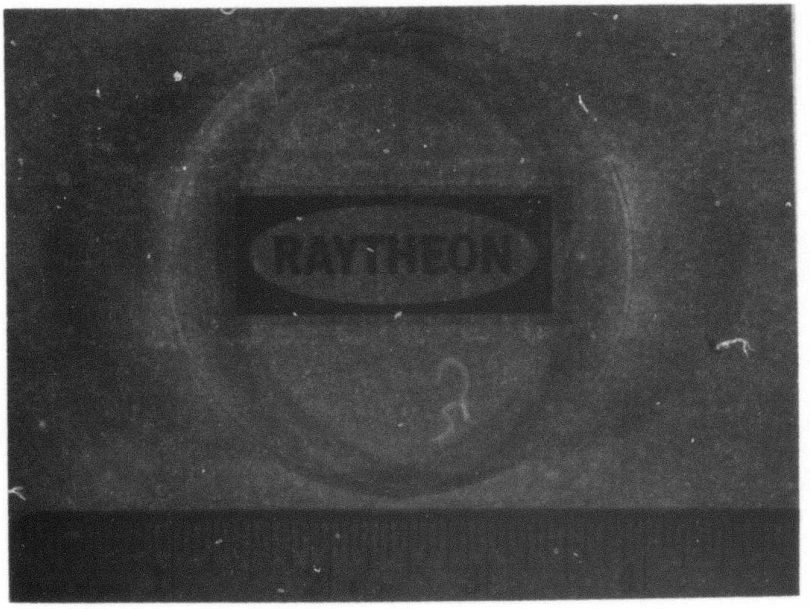

Fig. 1 Polished Casting of SrF_2 3 Inch Diameter × 1/2 Inch Thick.

when the VHP furnace was modified to include temperature control over the entire range necessary (room temperature to over 1500°C) as well as controlled cooling at rates as low as 10°C/hr. Bare wire Pt; Pt - 13 percent Rh thermocouples are used for temperature control, with an optical pyrometer being used as an auxiliary check of the temperature.

With such modifications, the present procedure for obtaining castings of SrF_2 and CaF_2 is as follows (for the vacuum hot press furnace): The charge to be melted (fluoride plus lead fluoride added as an oxide scavenger – usually 2 - 5 percent by weight) is loaded in a covered ATJ graphite crucible and placed in the furnace. The crucible rests on a PG (pyrolytic graphite) pedestal ("a" axis parallel to the desired direction of solidification) which in turn rests on the bottom water-cooled ram. A vacuum is drawn and, when it reaches 10^{-4} torr, the furnace is brought slowly up to temperature in about three hours. The charge is held at 1500°C for one hour to insure complete melting. During this time the water-coolant to the bottom pedestal is turned off to maximize the temperature. In the final 15 minutes of melting, the water coolant is turned on to establish a thermal gradient in the crucible from top to bottom, in order to promote unidirectional solidification. The furnace is then switched to controlled cooling at the desired rate by adjusting the clock-drive controls. After complete solidification is assured, the water-coolant to the pedestal is again turned off to minimize the thermal gradient in the ingot, and the cooling rate may be reset to the desired cooling to room temperature. The total process requires about three days in the case of SrF_2.

CaF_2 can be cooled more quickly and the process requires only one day. The castings produced in the above manner are still quite strained (probably due to residual thermal gradients in the furnace). Consequently, each sample must be subsequently strain annealed in the two-zone vacuum furnace prior to further handling.

Starting material for most castings was high purity, single crystal chips of CaF_2 (Optovac) or SrF_2 (Harshaw). However, several castings of CaF_2 and SrF_2 were made from in-house purified "reagent" grade powder with equal success. As listed in Tables 1 and 2, several purification schemes were used.

One has been discussed before,[1] using teflon vapors at elevated temperature according to the following thermodynamically favorable reaction:

$$2\ CaO + C_2F_{4(g)} \rightarrow 2\ CaF_2 + 2\ CO_{(g)} \quad .$$

The other procedure is to vacuum bake the "reagent" grade powder at 900°C to remove as much absorbed water as possible. The sintered powder can then be melted in the normal way with only lead fluoride being added as an oxide scavenger according to the reaction:

$$CaO + PbF_2 \rightarrow CaF_2 + PbO \quad ,$$

with the PbO and any excess PbF_2 being removed by volatilization at the elevated temperatures.

In purifying the "reagent" grade SrF_2 powder (obtained from Barium and Chemicals, Inc., Steubenville, Ohio), the latter procedure proved quite effective. In using the teflon vapor techniques, the teflon pyrolyzes (as is the case with CaF_2), but the resulting graphite contamination is difficult to remove by subsequent roasting in air at 500°C. In the purification scheme of the SrF_2 powder, it was noticed that the as-received material was contaminated with small black particles. X-ray diffraction proved the contamination to be iron – probably iron oxide because, on grinding, a reddish-brown powder resulted. Moreover, the particles are magnetic and are effectively removed by passing a magnet repeatedly through the powder. However, that some contamination is still present is obvious because the vacuum baked SrF_2 powder turns pink. Nonetheless, excellent results were obtained from such powder (VHP-335); on the other hand, using the teflon-treated powder subsequently roasted in air, one casting (VHP-329) was obtained with white precipitates scattered throughout. However, when it was remelted with additional lead fluoride added, good results were obtained (VHP-346 and 349). Teflon-treated CaF_2 gives consistently good results (VHP-307, 308, 309 and 317).

It was noticed that castings produced from the purified powder (both

SrF_2 and CaF_2) seemed to be sensitive to cracking by thermal shock (predominantly intergranular in nature). It may be due to trace residual impurities at the grain boundaries with increased sensitivity to thermal shock, as will be discussed below.

Selected samples of "reagent" grade CaF_2 were analyzed by emission spectroscopy (Jarrell-Ash, Waltham, Massachusetts). Table III shows the results of the analyses on the following samples: 1) As-received powder (Fisher Certified CaF_2), 2) A casting (VHP-272) using teflon-treated powder, and 3) A casting (VHP-273) using untreated powder. As can be seen, the teflon-treated material has the lowest impurity content, containing only alkaline earth impurities (Mg, Sr, and Ba). The untreated casting is somewhat improved over the as-received powder. Table IV gives the limits of detection of impurities in CaF_2 in the analyses.

As mentioned above, the castings of SrF_2 and CaF_2 prepared from purified "reagent" powder seemed quite susceptible to thermal shock cracking, being predominantly intergranular in nature. This behavior suggested weakened grain boundaries due to impurity precipitation and led to further investigation. Samples of three cast fluorides – BaF_2, SrF_2, and CaF_2 (VHP-147, 311, and 317, respectively) that failed intergranularly were investigated by X-ray microprobe analysis and SEM (scanning electron microscopy). Microprobe analysis of impurities and their distribution in these samples indicated a weak, uniformly distributed contamination of Al (in CaF_2 and BaF_2), Ca (in SrF_2), and Sr (in BaF_2). In addition, the grain boundary surfaces showed localized accumulations containing predominantly Na, S, Cl, K and occasionally also Mg, Si, Fe, and Zn. These accumulations seemed to be located in surface irregularities such as holes, cracks, and precipitates. To obtain a clearer correlation between surface appearance and impurity content, magnified maps of the grain boundary surfaces were produced from overlapping SEM pictures. Specific irregularities were identified and subjected to microprobe analysis, the results of which follow.

Figures 2 and 3 illustrate the example of BaF_2 (VHP-147). Figure 2a shows the general surface area with an irregularity at the intersection of two

TABLE III

ANALYSIS OF "REAGENT" GRADE CaF_2 SAMPLES

JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Company
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg Mr. Swift

DATE RECEIVED: 10/17/74
DATE REPORTED: 10/28/74
ORDER NO.: 90-77543

SAMPLE DESCRIPTION: CaF_2
INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

	1	2	3		1	2	3		1	2	3		1	2	3
Li	ND	ND	ND	Zn	ND	ND	ND	Sb	ND	ND	ND	Lu			
Be	ND	ND	ND	Ga	ND	ND	ND	Te	ND	ND	ND	Hf	ND	ND	ND
B	ND	ND	ND	Ge	ND	ND	ND	Cs	ND	ND	ND	Ta	ND	ND	ND
Na	800	ND	ND	As	ND	ND	ND	Ba	80	10	100	W	ND	ND	ND
Mg	10	5	10	Rb	ND	ND	ND	La				Re	ND	ND	ND
Al	.5	ND	1	Sr	400	400	600	Ce				Os	ND	ND	ND
Si	ND	ND	ND	Y				Pr				Ir	ND	ND	ND
K	ND	ND	ND	Zr	ND	ND	ND	Nd				Pt	ND	ND	ND
Ca	H	H	H	Nb	ND	ND	ND	Sm				Au	ND	ND	ND
Ti	ND	ND	ND	Mo	ND	ND	ND	Eu				Hg	ND	ND	ND
V	ND	ND	ND	Ru	ND	ND	ND	Gd				Tl	ND	ND	ND
Cr	.5	ND	ND	Rh	ND	ND	ND	Tb				Pb	ND	ND	ND
Mn	2	ND	ND	Pd	ND	ND	ND	Dy				Bi	ND	ND	ND
Fe	5	ND	.1	Ag	ND	ND	ND	Ho				Th			
Co	ND	ND	ND	Cd	ND	ND	ND	Er				U			
Ni	ND	ND	ND	In	ND	ND	ND	Tm				P	ND	ND	ND
Cu	5	ND	ND	Sn	ND	ND	ND	Yb				Se			

REMARKS: 1 = CaF_2 Powder (Fisher)
2 = VHP #272
3 = VHP #273
Results in ppm.

KEY:
ND - Not Detected
VVFT < .0001%
VFT .0001% - .001%
FT .001% - .01%
T .01 - .1%
L .1 - 1%
M 1% - 10%
H >10%

STAFF ANALYST

SUPERVISOR, TESTING LABS

TABLE IV

LIMITS OF DETECTION FOR ANALYSIS OF CaF_2 SAMPLES

JARRELL-ASH DIVISION
Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co.
28 Seyon St.
Waltham, MA 02154
ATTN: Mr. R. Newberg

DATE RECEIVED: 10/17/74
DATE REPORTED: 11/27/74
ORDER NO.:

SAMPLE DESCRIPTION: Limits of Detection in CaF_2 in ppm
INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

		x				x				x				x	
Li	25	1		Zn	10			Sb	5			Lu			
Be	.1			Ga	1			Te	40			Hf	50		
B	1			Ge	1			Cs	25	1		Ta	50		
Na	10	.5		As	25			Ba	5			W	50		
Mg	.01			Rb	10	1		La				Re	20		
Al	.1			Sr	5			Ce				Os	20		
Si	.1			Y				Pr				Ir	20		
K	50	1		Zr	20			Nd				Pt	5		
Ca				Nb	40			Sm				Au	2		
Ti	1			Mo	2			Eu				Hg	50		
V	5			Ru	10			Gd				Tl	50		
Cr	1			Rh	5			Tb				Pb	.5		
Mn	.1			Pd	5			Dy				Bi	1		
Fe	1			Ag	.01			Ho				Th			
Co	5			Cd	1			Er				U			
Ni	1			In	1			Tm				P	25		
Cu	.05			Sn	.5			Yb				Se			

REMARKS: x = Separate analysis looking at high wavelength lines

KEY:

ND - Not Detected		T	.01 - .1%
VVFT	< .0001%	L	.1 - 1%
VFT	.0001% - .001%	M	1% - 10%
FT	.001% - .01%	H	>10%

C. Bonini
STAFF ANALYST

C. Bonini
SUPERVISOR, TESTING LABS

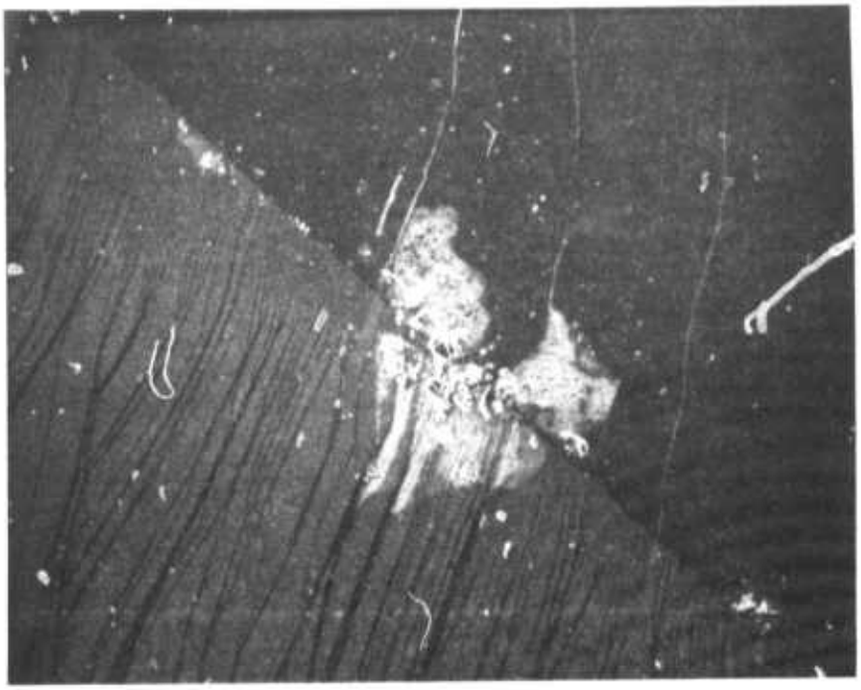

Fig. 2a Fracture Surface of Cast BaF_2 Sample. SEM 200×

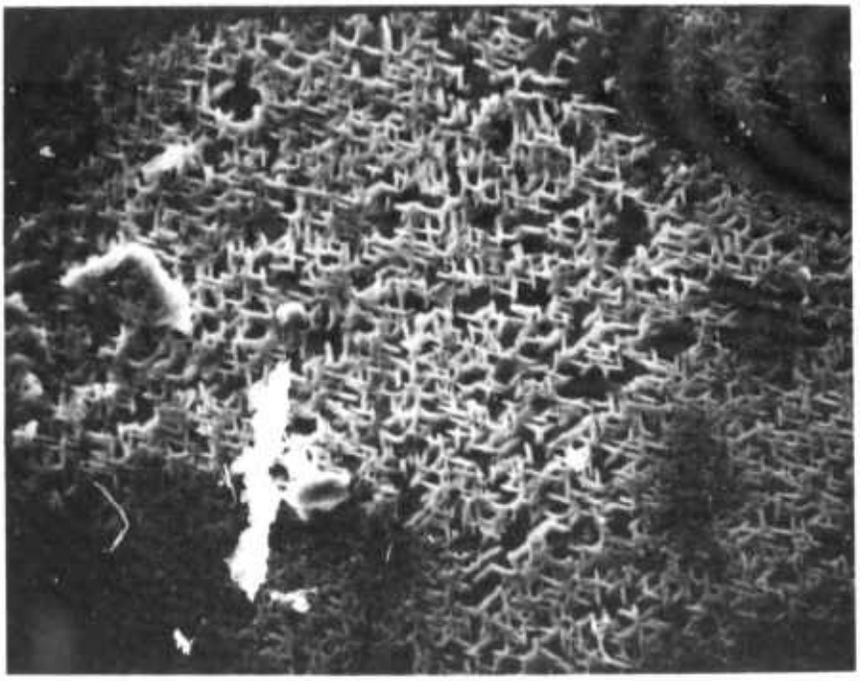

Fig. 2b Precipitate Area at Fracture Surface of Cast BaF_2 Sample. SEM 2000 ×

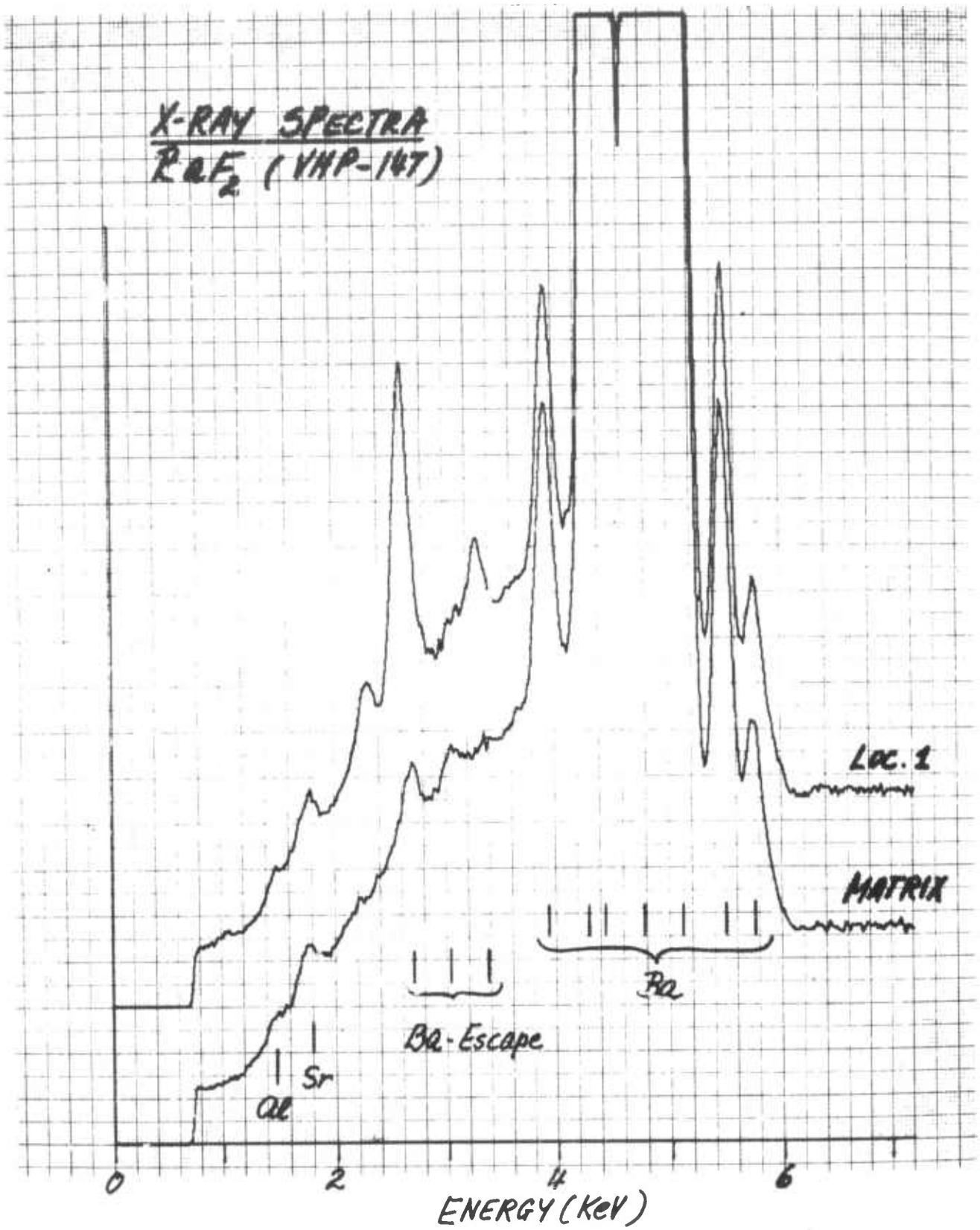

Fig. 3a X-Ray Spectra of Cast BaF_2 Sample

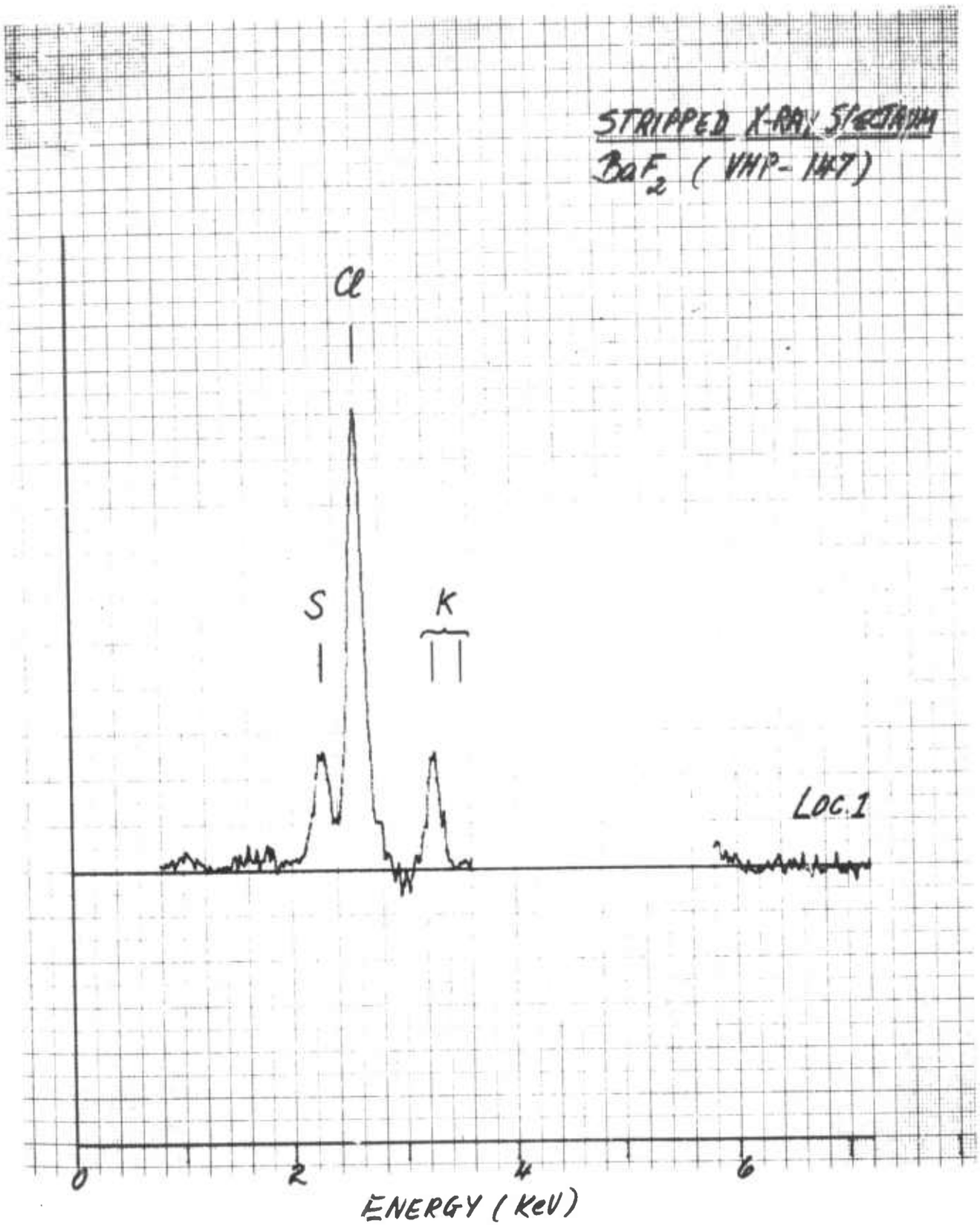

Fig. 3b Stripped X-Ray Spectrum of Cast BaF Sample

grains. The precipitate is shown at higher magnification in Fig. 2b. Care was taken to avoid contamination of the surfaces during handling, but it is not entirely clear in this case if the precipitate is not a result of handling. Figure 3a is the overall X-ray spectra from microprobe analysis of both the general uniform distribution of the grain boundary surface (designated matrix) and the precipitate (designated location 1). Figure 3b is the stripped X-ray spectrum of the precipitate; i.e., the matrix spectrum is subtracted from the precipitate spectrum. Any differences in impurity concentrations between the two are shown as sharp peaks in the stripped spectrum. In this case the precipitate is enriched in K, S, and Cl.

Similarly, Figs. 4a and 4b show the grain boundary fracture surface of SrF_2 (VHP-311) with several irregularities and a magnification of a similar irregularity, respectively. Such irregularities appear to be precipitates torn from the matrix during fracture and are clearly not contaminants from handling. Figures 5a and 5b show the X-ray spectra for the two areas – the matrix (no precipitates probed) and precipitate (designated location 1) and the stripped spectrum of location 1, the latter showing the area to be enriched in Na, K, and Cl.

Finally, Figs. 6a -e show similar grain boundary surfaces of cast CaF_2 (VHP-317) and three quite different surface irregularities (designated locations 1, 2, and 3 in the X-ray spectra of Figs. 7a and 7b). It can also be noted (Figs. 6a and 6b) by the ripply effect of the general surface that true intergranular failure occurred, whereas for the BaF_2 and SrF_2, cleavage steps are also present. From the X-ray spectra of Fig. 7a it can be seen that the CaF_2 matrix has few impurities. However, the irregularities are quite rich and substantially different from each other, as best seen in the stripped X-ray spectra of Fig. 7b. The protruding mass of location 1 is enriched mainly in Mg, Al, Si, and Fe; while what appears to be a hole at location 2 is enriched in Si, S, Cl, and K. Finally, the white precipitate at location 3 is enriched mainly in Na, Si, Cl, and K.

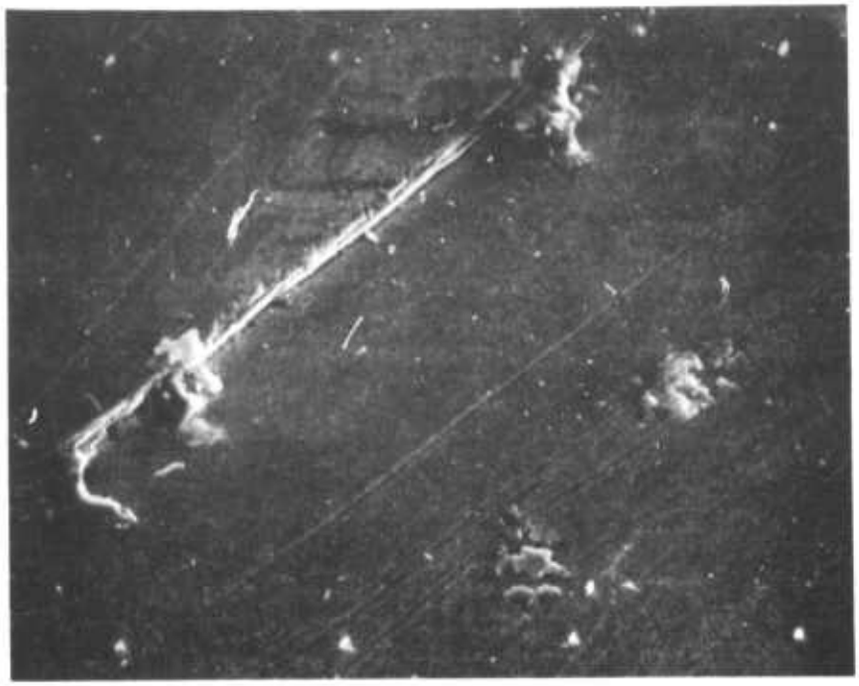

Fig. 4a Fracture Surface of Cast SrF_2 Sample. SEM 700 ×

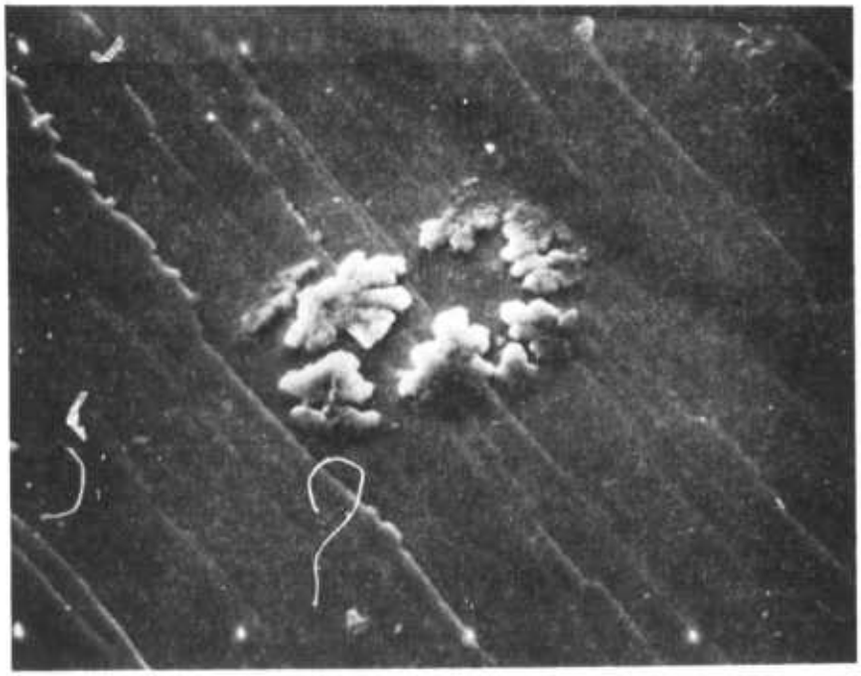

Fig. 4b Fracture Surface of Cast SrF_2 Sample. SEM 2000 ×

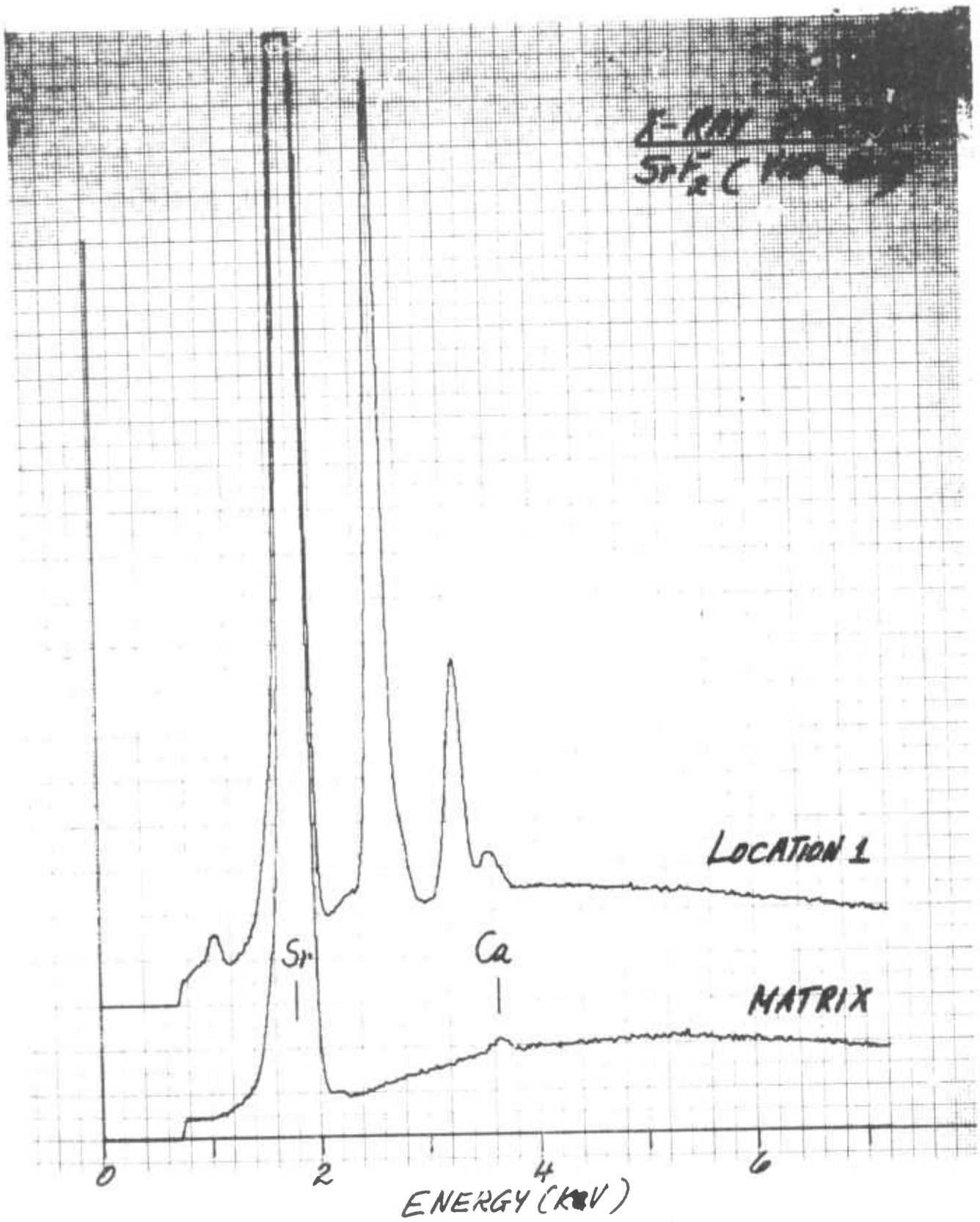

Fig. 5a X-Ray Spectra of Cast SrF_2 Sample

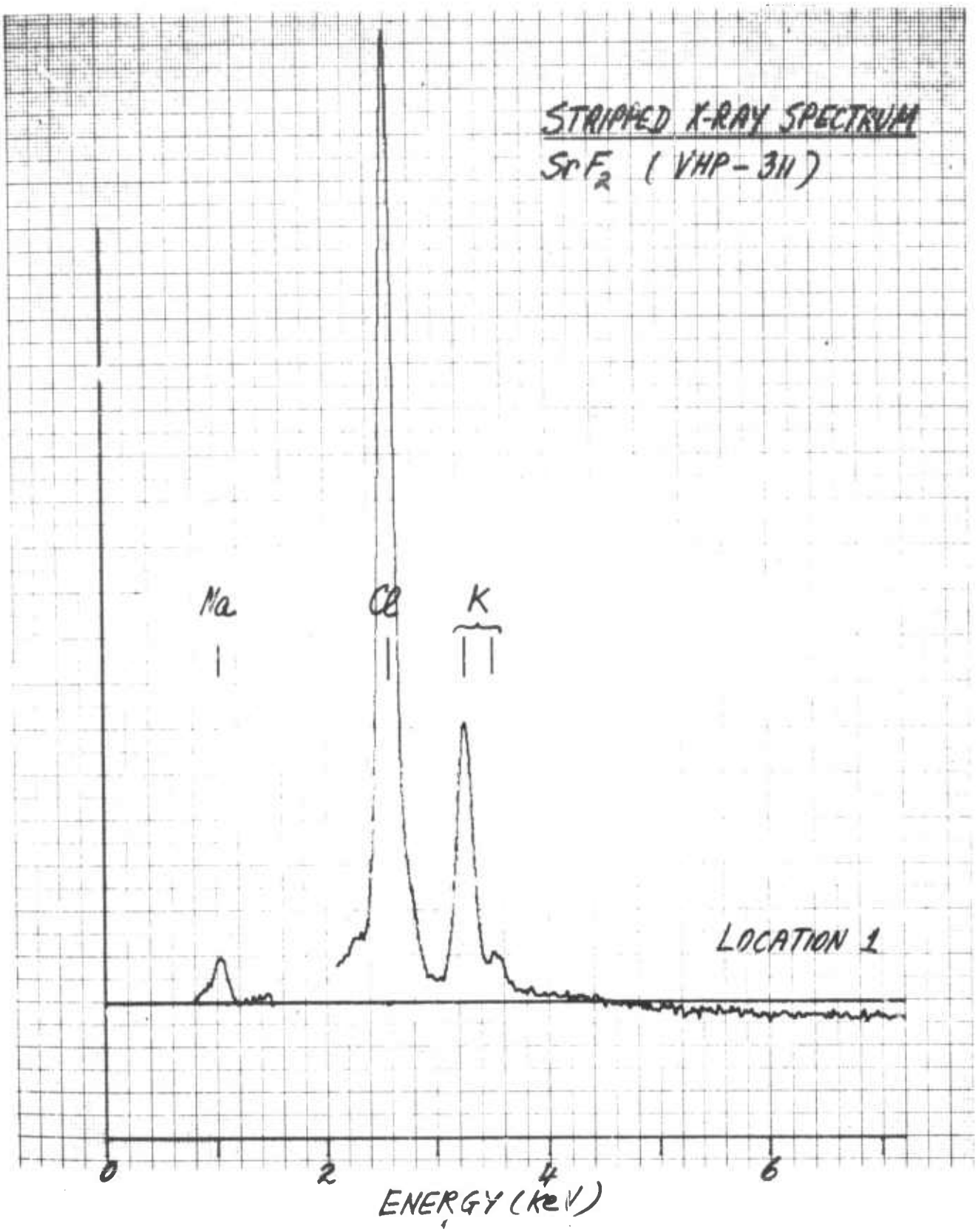

Fig. 5b Stripped X-Ray Spectrum of Cast SrF_2 Sample

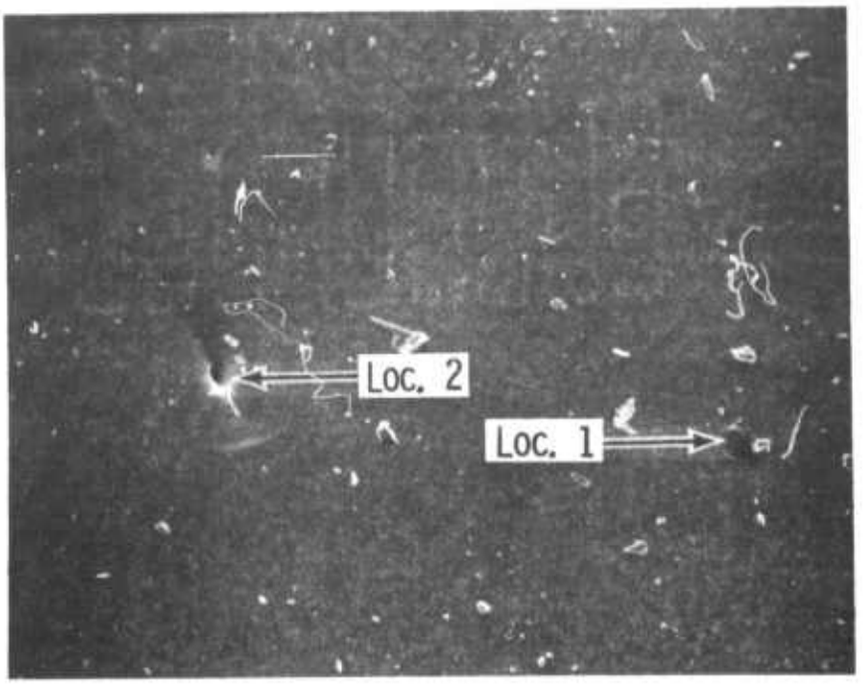

Fig. 6a Fracture Surface of Cast CaF_2 Sample. SEM 100 ×

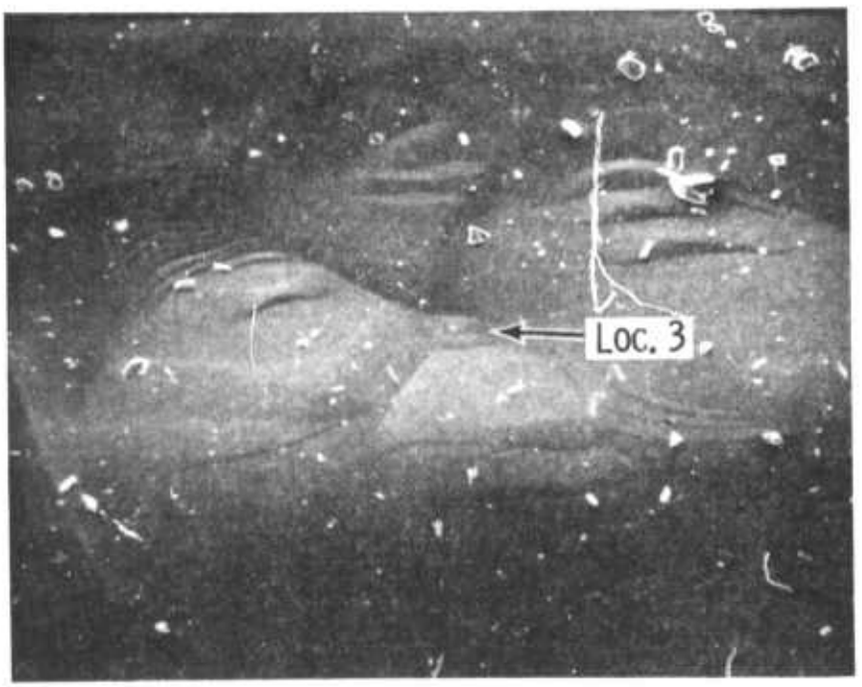

Fig. 6b Fracture Surface of Cast CaF_2 Sample. SEM 100 ×

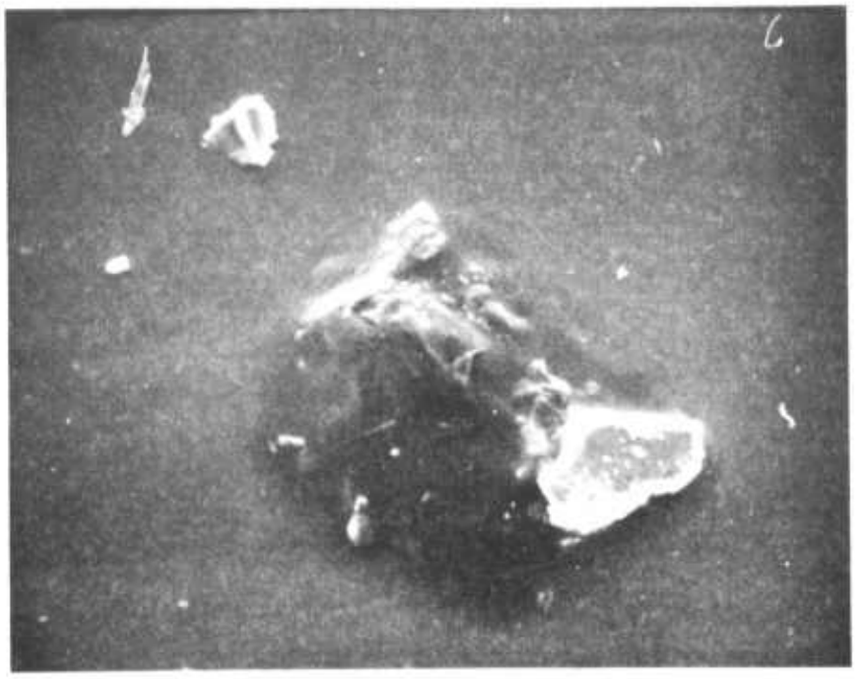

Fig. 6c Location 1. SEM 1000 ×

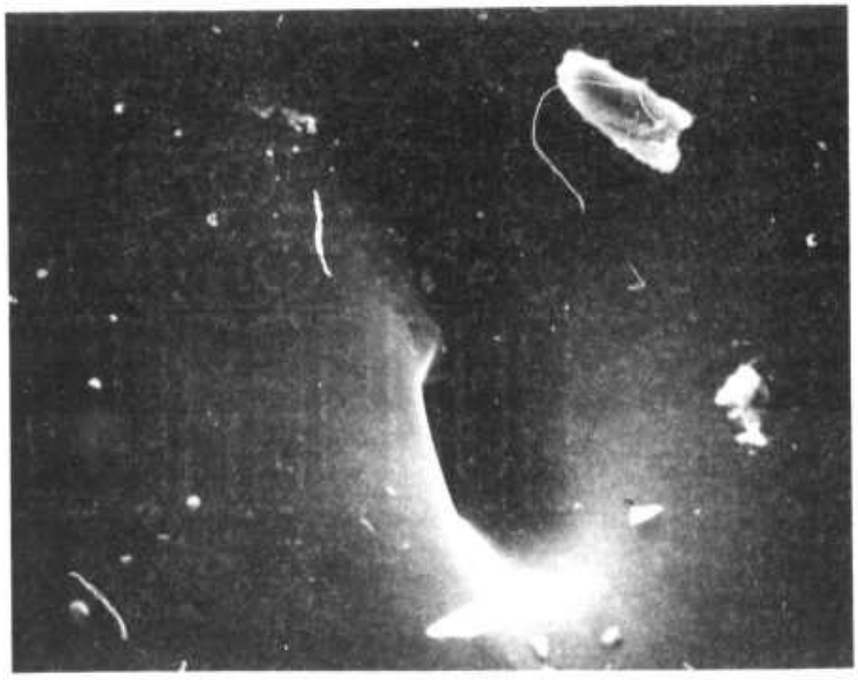

Fig. 6d Location 2. SEM 1000 ×

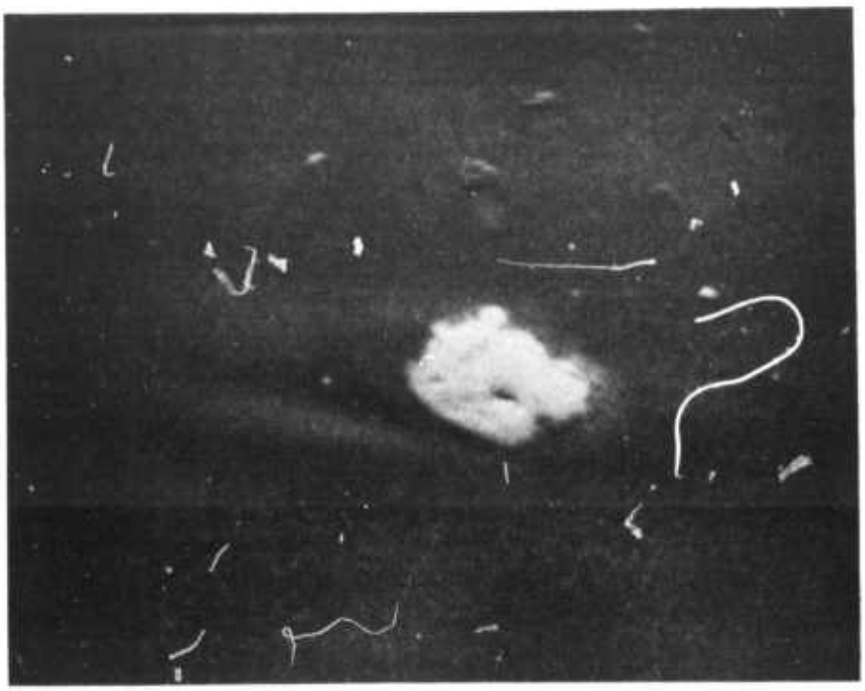

Fig. 6e Location 3. SEM 3000 ×

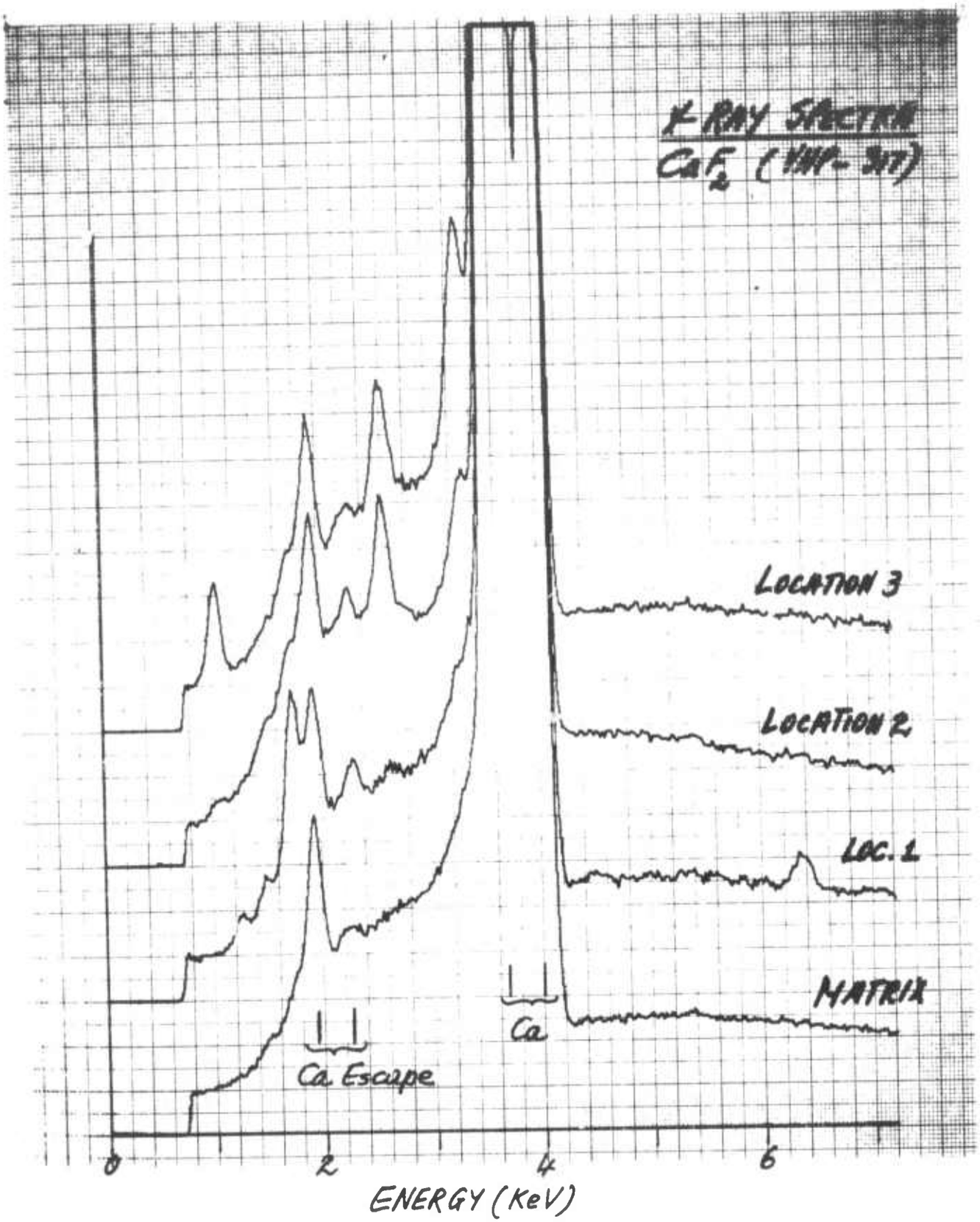

Fig. 7a X-Ray Spectra of Cast CaF_2 Sample

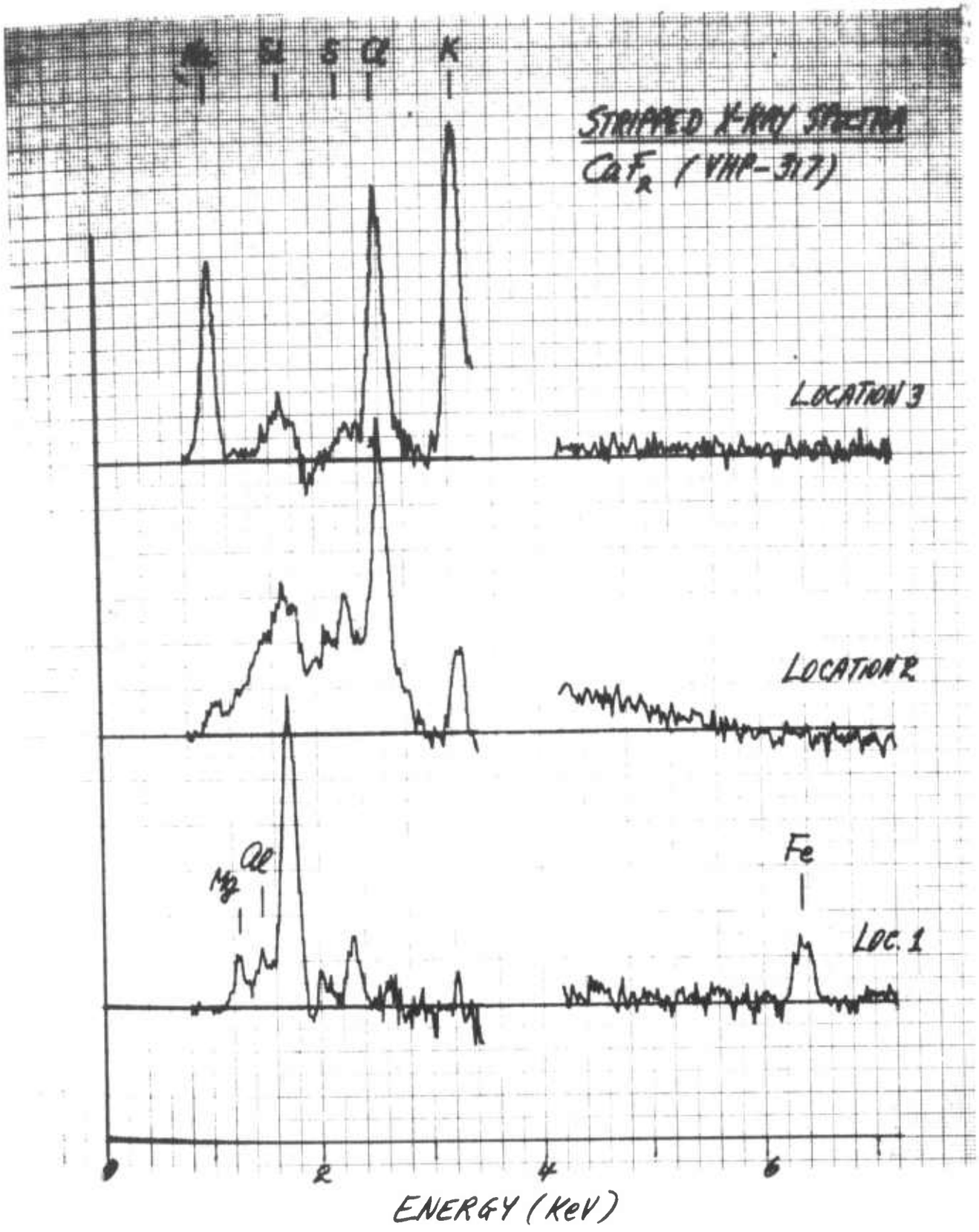

Fig. 7b Stripped X-Ray Spectra of Cast CaF_2 Sample

The above results indicate that the bulk of the contamination is localized in accumulations at the grain boundaries. Whether or not these impurities seriously affect the mechanical properties (such as thermal shock resistance) is not quantitatively known. Further effort is being planned to fully evaluate their effect.

2.2 Inert Atmosphere Casting

During the last quarter, work was initiated to develop a casting technique in an inert atmosphere instead of the high vacuum (10^{-4} torr or better) required normally. The advantage of inert atmosphere operation is that unidirectional solidification may be better accomplished due to the better heat transfer provided by the gas. It is also desirable because, in the event of scale-up to larger sizes, an inert atmosphere may be less expensive and more convenient to provide than a high vacuum system.

A series of castings of CaF_2 were attempted in the vacuum hot press furnace using dry, high purity argon (passed over titanium chips at 800 - 900°C to remove residual H_2O and O_2) to provide partial pressures of 1, 5, 15, 25, and 50 torr. The castings are listed in Table 1. As expected, better heat transfer resulted in complete unidirectional solidification in all but two of the castings (VHP-301 and 317). However, except for these same two castings, the inert atmosphere castings were all slightly discolored (a yellowish to bluish tinge) indicating that the atmosphere was not sufficiently inert and that there was impurity pickup in the castings (probably O_2). Further attempts are presently under way to improve the technique.

2.3 Hot Forging

During the last quarter only two hot forgings were attempted, as listed in Table 1. One-inch diameter samples were core drilled from a polycrystalline casting of CaF_2 (VHP-269) and hot forged at 1000°C to 81 percent and 75 percent reduction in thickness (VHP-302 and 303) in the vacuum hot press furnace. Both were successfully forged, but, as was the case with hot forged

single crystal samples of CaF_2,[1] the resultant grain size was large (on the order of several millimeters) due to the high forging temperature. No further work on hot forging is presently being planned because of the very good mechanical properties of the castings as will be discussed later.

2.4 Strain Annealing

One of the major problems with the fusion casting of the fluorides is the residual strain present in the ingots cast in the vacuum hot press furnace, due to rapid or uneven cooling. The problem was alleviated somewhat, as mentioned earlier, by the furnace modification allowing controlled cooling to room temperature from the solidification temperatures. However, the cast ingots still come out strained and must be strain-annealed prior to subsequent handling. The strain annealing procedure that has been used during the third quarter is the same as that developed during the first two quarters, i.e., annealing at 900°C for 10 hours followed by controlled cooling at 25°C/hr to room temperature. Samples of cast SrF_2 thus annealed show marked strain reduction, but as Fig. 8 illustrates, the procedure is not entirely successful in producing strain-free material. Further work is presently under way to develop a more satisfactory strain anneal for SrF_2. Nevertheless, with the strain reduction presently achieved, further handling of the cast ingots can be done, e.g., core drilling, cutting, grinding, and polishing, without marked susceptibility to cracking.

Also during the third quarter, a large Lindberg box furnace was installed in the laboratory. It has heating and cooling capabilities at controlled rates of about 10 - 100°C/hr (subject to the natural heating and cooling rates of the furnace) from room temperature to 1500°C.

By using an Inconel inert atmosphere retort (approximately $10 \times 10 \times 12$ inches inner dimensions) preliminary strain anneal runs were attempted in this furnace. Samples were one-inch diameter single crystals of CaF_2 (Optovac). The procedure for each heat treatment was to heat the furnace at 50°C/hr to

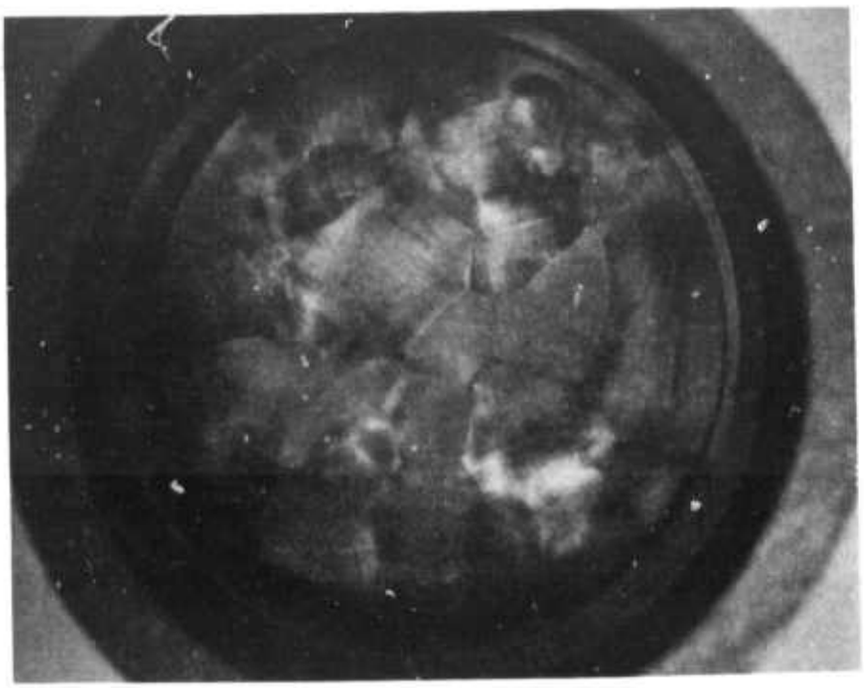

Fig. 8 Cast SrF_2 (VHP-343) After 900°C Anneal for 10 hrs. and Cooled at 25°C/hr. Viewed through crossed polarizers.

the soak temperature after purging the system as desired. The soak temperature (800, 900, or 1000°C) was held for ten hours, followed by cooling at 25°C/hr to room temperature. Table V presents the results of these runs. The samples heated in air or argon at 1000°C showed fine white precipitates distributed either uniformly throughout (opacity) or as veils. Samples heated in argon or helium without sufficient purging at 900°C also showed some opacity. However, samples annealed at 800 or 900°C and properly purged with argon were as transparent as before and showed no scattering (as viewed with a He-Ne laser beam).

2.5 Optical Properties

The feasibility of casting consistently high quality SrF_2 and CaF_2 has been demonstrated by using either high purity single crystal chips or purified "reagent" grade powder as starting material. Laser calorimeter measurements at 5.25μm are summarized in Table VI for both CaF_2 and SrF_2. The 5.25μm apparent absorption coefficients of cast CaF_2 ingots fall consistently near 4.5×10^{-4} cm^{-1} (14 measurements on 10 castings), quite near the value of 1.8×10^{-4} cm^{-1} predicted from the exponential law. No surface corrections have been made for these measurements on CaF_2.

Figure 9 shows the total absorption at 5.25μm versus length plot for a series of Harshaw single crystal samples of SrF_2 as reported by Deutsch[2] with the 5.25μm absorption coefficient being 4.1×10^{-5} cm^{-1} and a surface loss value of 3.9×10^{-5} per surface. In the same figure are also plotted several measurements on polycrystalline cast SrF_2. They fall very near the line for single crystal material and have a 5.25μm absorption coefficient of 3.5×10^{-5} cm^{-1} with a surface loss value of 4.3×10^{-5} per surface, results essentially the same as for single crystal material, and which are very near the predicted value of 2×10^{-5} cm^{-1}.

These results show clearly that for both SrF_2 and CaF_2, the fusion casting process does not degrade the optical properties of high purity single crystal starting material. Furthermore, it proves that an all graphite system is capable of achieving high quality material and that polycrystalline material is equivalent in optical quality to single crystal material.

TABLE V

EFFECT OF HEAT TREATMENT OF CaF_2 SINGLE CRYSTALS

Heat Treatment Temperature (°C)	Atmosphere	Comments
1000	Air	Sample opaque
900	Argon (unpurged)	Sample uniformly hazy
900	Helium (unpurged)	Sample uniformly hazy
1000	Argon (purged 24 hrs.)	Veils throughout
900	Argon (purged 24 hrs.)	No haziness or scatter
800	Argon (purged 24 hrs.)	No haziness or scatter

TABLE VI

SUMMARY OF FLUORIDE MEASUREMENTS

Material	$\beta_{measured}$ 5.25μm	Surface Correction	$\beta_{predicted}$ Exponential Law
Optovac CaF_2	$4.7 \pm 0.3 \times 10^{-4}$cm	No	1.8×10^{-4}cm^{-1}
Cast CaF_2	$4.5 \pm 0.3 \times 10^{-4}$	No	
Harshaw SrF_2	$4.1 \pm 0.7 \times 10^{-5}$*	Yes	2×10^{-5}
Cast SrF_2	3.5×10^{-5}	Yes**	

* From reference (2), surface correction of loss is $3.9 \pm 0.9 \times 10^{-5}$ per surface.

** Surface correction of loss is 4.3×10^{-5} per surface.

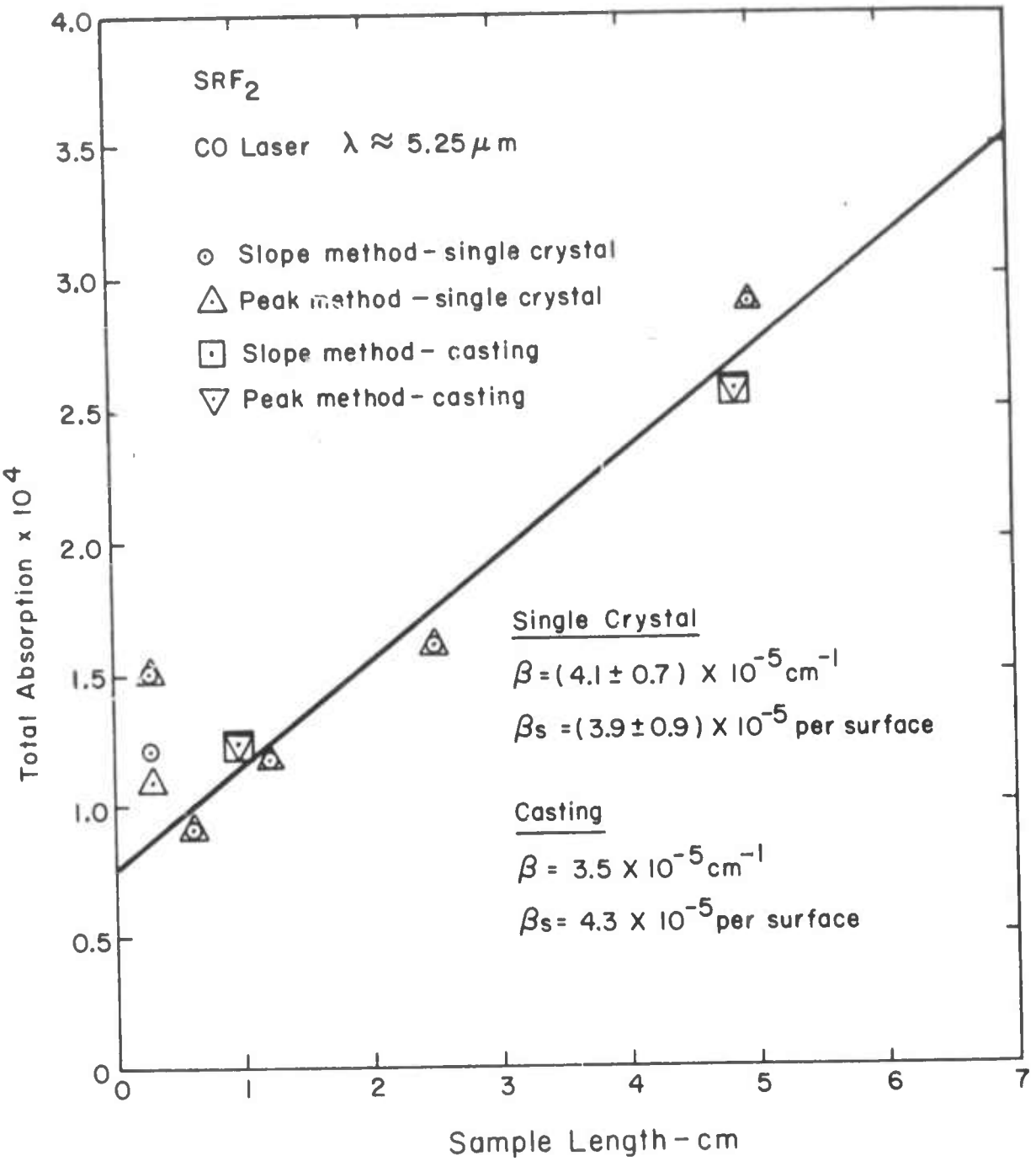

Fig. 9 Total Absorption versus Length for SrF_2 at 5.25μm

For the samples of CaF_2 single crystals heat treated in the Lindberg box furnace, the results are as follows: For the samples annealed in purified argon at either 800 or 900°C (sufficiently purged), no increase in the 5.25μm apparent absorption coefficient ($4.7 \pm 0.3 \times 10^{-4}$ cm^{-1}) was measured as compared to unannealed single crystal CaF_2. At 1000°C (in argon) an increase is observed (1.2×10^{-3} cm^{-1}) with a corresponding increase in scattering (as viewed with a He-Ne laser). These results correlate with those reported earlier on vacuum (10^{-2} - 10^{-3} torr) annealing at 800, 900 and 1000°C.[1] In both cases it now seems clear that the systems are not sufficiently O_2-free, but that the damaging reactions occur only above 900°C, at least within the time period of these runs (10 hours) and with the low but unknown O_2 concentration present.

For those samples of CaF_2 cast with a partial pressure of argon (inert atmosphere of 1 - 50 torr) present, the samples were typically discolored as mentioned previously. One sample (VHP-318) that was discolored a faint yellow-blue had a measured 5.25μm apparent absorption coefficient of 5.8×10^{-3} cm^{-1}; another similarly cast sample (VHP-317 - 50 torr argon) was colorless with a very good apparent absorption coefficient of 4.1×10^{-4} cm^{-1}. However, another colorless sample (VHP-301 - 25 torr argon) was higher, with $1.11 \pm .06 \times 10^{-3}$ cm^{-1}. Clearly the results are mixed and further work is necessary to improve the technique.

2.6 Mechanical Properties

Preliminary mechanical property measurements have been obtained on CaF_2 and SrF_2. Fracture strength as a function of surface preparation was determined for single crystal CaF_2 and polycrystalline cast CaF_2 and SrF_2. The stress strain curves were determined in three-point bending on an Instron universal testing machine. The sample span was one inch and the cross-head speed was 0.05 cm/ min. Nominal sample cross sections were 3/ 16 × 3/ 16 inches. Test bars were obtained from annealed ingots by cutting and polishing and were tested immediately or were either chemically polished in concentrated H_2SO_4 or annealed prior to testing. Sample dimensions were measured after testing to prevent surface damage. Grain size for the polycrystalline cast samples is generally on the order of one cm. In all cases fracture occurred with no apparent yielding.

The results as presented in Table VII show the effects of polishing and annealing on the fracture strength of CaF_2, and indicate qualitatively the large effect surface preparation has. By going from a rough polish (wet 600 grit grinding paper – Fig. 10) to a normal in-house laboratory polish (Fig. 11) or to an optical polish (polished on a pitch lap by an optician) as shown in Fig. 12, the strength of cast CaF_2 is raised from 6590 psi to 8590 psi to 13570 psi, respectively. Moreover, the normal polished samples which were chemically polished prior to testing (calculated to remove about 1×10^5 Å from each surface) also show a marked increase in strength to 12670 psi. Note that rough polished single crystal CaF_2 has a strength equivalent to the rough polished cast CaF_2, an expected result because of the large grain size of the castings. These polishing results indicate that strength is limited by surface flaws. Damaging flaws may be removed in part either by more careful mechanical polishing or by chemical polishing.

Further evidence is seen in the effect of annealing of individual test bars which also significantly increases the fracture strength. Specimens similarly polished as above were annealed prior to testing. In all three instances (rough polished single crystal, normally polished cast, and optically polished cast CaF_2 samples) the fracture strengths have increased – to 15700, 16800, and 22800 psi's, respectively. Evidently by annealing the test bars, some surface damage is either reduced or removed, a further indication that the fracture strength of CaF_2 is limited by surface flaws. This assumes that bulk strain in all the bars are the same, supported qualitatively by viewing each specimen between crossed polarizers before testing and noting no differences. That is, all test bars appear macroscopically strain-free, whether they are to be tested as-polished or as-annealed (polished then subsequently annealed).

In all the above cases, fracture was predominantly transgranular in nature (i.e., cleavage). However, in the cases of samples of cast CaF_2 which were taken from castings annealed in the degrading anneal procedure[1] (1000°C in vacuum of 10^{-2} - 10^{-3} torr) fracture was totally intergranular in nature and strengths were reduced to 4740 ± 610 psi (normal polished samples) from 8590 psi. However, even in this instance, surface damage is limiting, since similar samples which were subsequently chemically polished show an increased

TABLE VII

FRACTURE STRENGTH OF CaF_2 †

Single Crystal[1]	Cast[1]	Cast[2]	C. P. Cast[2]	Cast[3]	Annealed* Single Crystal[1]	Annealed** Cast[2]	Annealed** Cast[3]
2900	5700	9500	14900	14900	13200	10900	21900
5700	7700	7900	10400	11900	16700	20600	26000
3000	6200	8300	12300	14500	17000	17500	22200
2600	--	--	--	15400	--	--	20700
8100	--	--	--	13300	--	--	--
--	--	--	--	10800	--	--	--
4950	6590	8590	12670	13570	15730	16830	22800
±2190	±850	±680	±1850	±1660	±1730	±4080	±1990

[1] Rough polish

[2] Normal polish

[3] Optical polish

* 7 hrs. at 1075°C in 10^{-5} torr vacuum

** 10 hrs. at 900°C in 10^{-3} torr vacuum

C. P. ≡ chemical polish 12 min. in conc. H_2SO_4 as final treatment before testing

† Measured in psi.

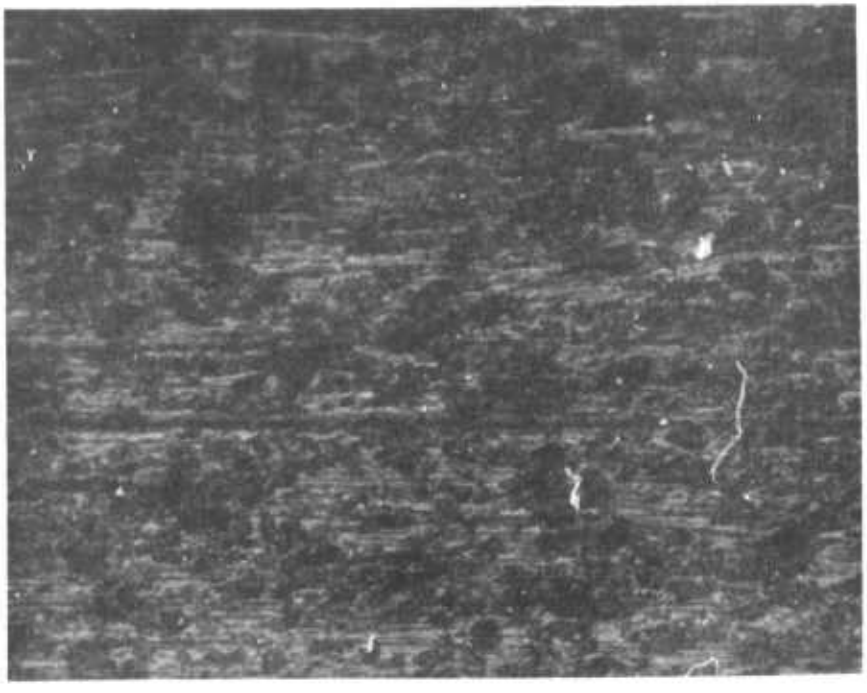

Fig. 10 Surface of CaF_2 Sample After Rough Polish (600 grit SiC Paper) 187 ×

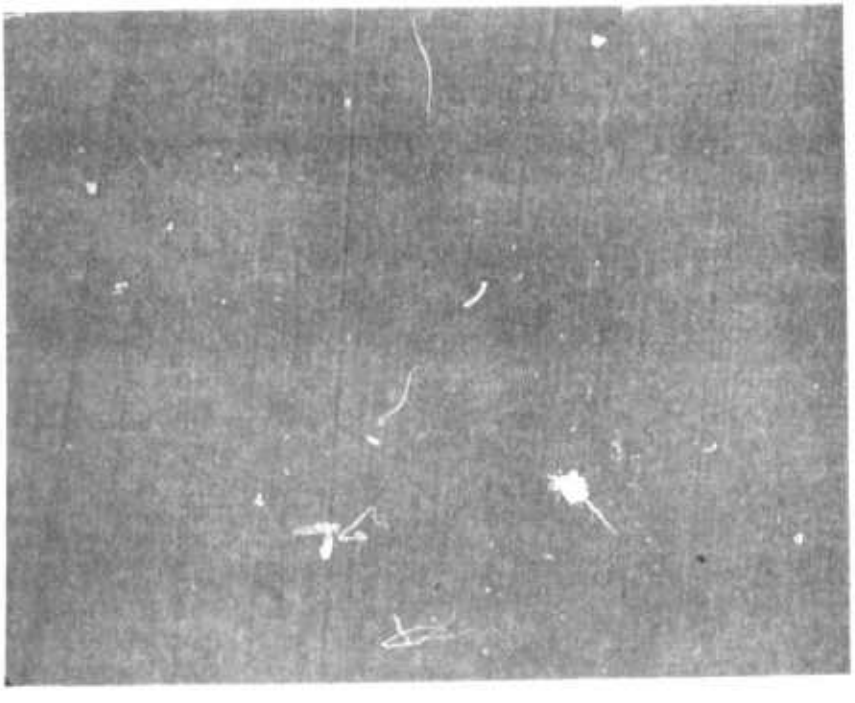

Fig. 11 Surface of CaF_2 Sample After Laboratory Polish. 187 ×

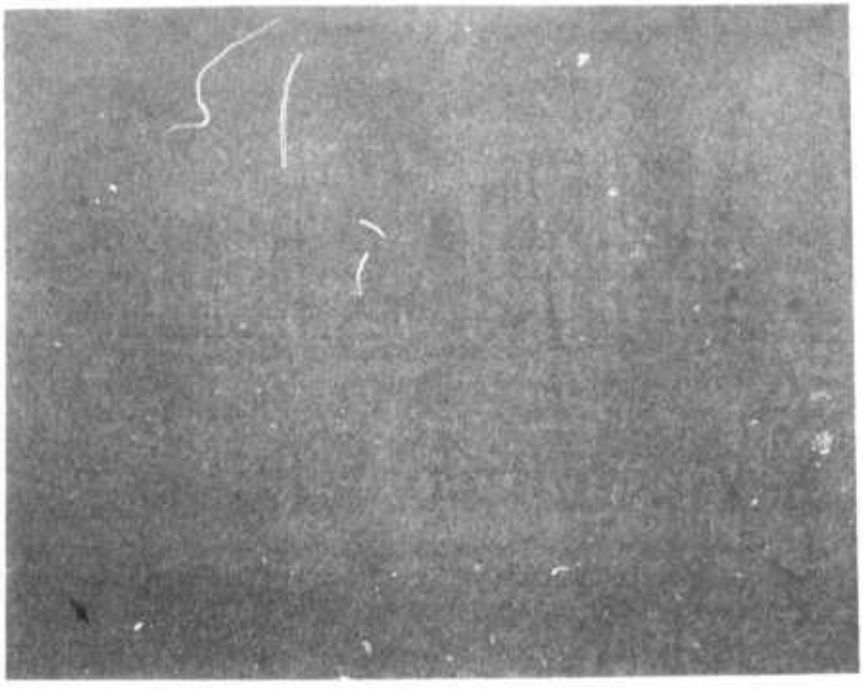

Fig. 12 Surface of CaF_2 Sample After Optical Polish (Pitch Lap). 187 ×

strength to 6480 ± 1310 psi, but still far below the 12670 psi level of similar specimens cut from castings annealed at 900°C. Thus it appears that annealing procedure not only degrades the optical properties but also significantly affects the mechanical properties. Since fracture is intergranular, it suggests grain boundary weakening as a result of an impurity precipitation problem as previously discussed.

The preliminary results for cast SrF_2 samples show a similar surface damage relationship. Samples tested as-polished (normal laboratory polish) show a strength of 12000 ± 4600 psi. Those samples subsequently annealed (900°C in 10^{-2} - 10^{-3} torr vacuum) show an increased strength to 17600 ± 2700 psi. These results also show that SrF_2 is equivalent in strength to CaF_2.

Hardness measurements were also taken on samples of CaF_2 and SrF_2. Hardness is determined with a Vickers DPH indenter and a 50 gm load mounted on a Vickers M-55 metallograph. The results that appear in Table VIII show that there is no difference in hardness in single crystal or cast material for either SrF_2 or CaF_2 and that CaF_2 is slightly harder than SrF_2.

TABLE VIII

VICKERS HARDNESS* OF CaF_2 AND SrF_2

	SrF_2	CaF_2
Single Crystal	171 ± 2	191 ± 2
Polycrystalline Cast	173 ± 1	194 ± 2

* Vickers Hardness Number, 50 gram load; average of four measurements.

3.0 SUMMARY AND CONCLUSIONS

3.1 Casting

Consistently high quality castings of both CaF_2 and SrF_2 have been fabricated regardless of the starting materials. That is, either high purity single crystal chips or pre-treated (vacuum baked or RAP-reactive atmosphere processing – treated in teflon vapors) "reagent" grade powder can be used as starting material to yield equivalent castings.

Castings of CaF_2 were attempted in an inert atmosphere – partial pressures of argon from 1 - 50 torr. The advantage is that unidirectional solidification is better accomplished because of the better heat transfer provided by the gas. The procedure needs more refinement because the castings are typically discolored.

3.2 Hot Forging

Preliminary hot forgings of polycrystalline cast CaF_2 have been done at 1000°C. At this high temperature a large grain size results so that not much advantage in grain size reduction is gained.

3.3 Optical Properties

5.25μm calorimetric apparent absorption coefficients of cast CaF_2 have been consistently obtained near 4.5×10^{-4} cm^{-1} regardless of the starting material. Those castings of CaF_2 fabricated in an inert atmosphere of argon have 5.25μm apparent absorption coefficients typically greater than 1.0×10^{-3} cm^{-1}, although one was as low as 4.1×10^{-4} cm^{-1}.

Using surface loss corrections, the 5.25μm absorption coefficient of cast SrF_2 is 3.5×10^{-5} cm^{-1}, very near the value of 2×10^{-5} cm^{-1} predicted from the exponential law.

3.4 Mechanical Properties

Mechanical measurements on cast CaF_2 show average fracture strengths ranging from a minimum near 6600 psi to near 23000 psi, depending on both the quality of polished surfaces and whether or not the polished test bars are subsequently annealed at 900°C (a strain relief procedure). This dependence is evidence that fracture is determined by surface flaws. Preliminary results for cast SrF_2 show average fracture strengths equivalent to cast CaF_2.

4.0 PLANS FOR NEXT QUARTER

Work during the fourth quarter will include the following areas of effort:

1. Continue the investigation of purification treatments of "reagent" grade starting powder for fluoride castings;

2. Continue the development of a casting procedure in an inert atmosphere;

3. Continue the mechanical property evaluation of single crystal and cast fluorides (SrF_2 and CaF_2);

4. Continue the evaluation of different annealing procedures, especially inert atmosphere operations at lower temperatures;

5. Investigate the effect of aliovalent additions to the fluorides under controlled casting conditions.

5.0 REFERENCES

1. R. T. Newberg and J. Pappis, "Casting of Halide and Fluoride Alloys for Laser Windows," Semiannual Technical Report No. 1, Contract No. F19628-74-C-0148 (December 1974).

2. T. F. Deutsch, "Research in Optical Materials and Structures for High Power Lasers," Final Technical Report, Contract No. DAAH01-72-C-0194 (December 1973).